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Letter

# First-principles electronic structure calculations of $\text{Ba}_5\text{Si}_2\text{N}_6$ with anomalous $\text{Si}_2\text{N}_6$ dimeric units

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## Abstract

First-principles band structure calculations were performed for the ternary alkaline-earth silicon nitride  $\text{Ba}_5\text{Si}_2\text{N}_6$  using the LSW method. The calculations show that both the (zero-)dimensionality of the  $[\text{Si}_2\text{N}_6]^{10-}$  dimeric units present in this structure and the coordination number of nitrogen by silicon have strong influences on the local electronic structure of these atoms. The interaction between the semicore-level states Ba 5p and N 2s is significant. Finally the compound is calculated to be a semiconductor with an indirect gap of 0.7 eV. The top of the valence band is dominated by the 2p states of the  $\text{N}^{[1]}$  atoms. The conduction bands are determined by N 3s states hybridized with Ba 6s states. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Nitride materials; Electronic band structure

Last years a number of new alkaline-earth silicon nitrides have been reported with intriguing crystal chemistry [1–3]. Some of them have very peculiar structures.  $\text{Ba}_5\text{Si}_2\text{N}_6$  is one of them.

The ternary alkaline earth silicon nitride  $\text{Ba}_5\text{Si}_2\text{N}_6$  was first synthesized by Yamane and DiSalvo [4]. They also determined the crystal structure from single crystals of the compound by X-ray diffraction.  $\text{Ba}_5\text{Si}_2\text{N}_6$  is orthorhombic, space group  $P2_12_12_1$ , with  $a=6.159$ ,  $b=10.305$ , and  $c=15.292$  Å, and  $Z=4$ . All the atoms occupy the general 4c sites. The five crystallographically different Ba atoms in the structure are coordinated by four to six nitrogen atoms [4]. Both silicon atoms are coordinated tetrahedrally by nitrogen atoms. The structure is built from isolated  $[\text{Si}_2\text{N}_6]^{10-}$  units, best described as two edge-sharing  $\text{SiN}_4$  tetrahedra (Fig. 1). There are six crystallographically different types of nitrogen atoms in the structure. As shown in Fig. 1, two of the six N atoms bridge the Si atoms ( $\text{NSi}_2$ , or  $\text{N}^{[2]}$  in short) with the N–Si distances of about 1.81–1.84 Å [4], which are larger than the  $\text{N}^{[2]}$ –Si distances in  $\text{MgSiN}_2$  [5], as well as in  $\text{M}_2\text{Si}_5\text{N}_8$  ( $\text{M}=\text{Ca}$ ,

Sr, Ba) compounds [6,7]. The other four N atoms are connected to only one Si atom ( $\text{NSi}$ , or  $\text{N}^{[1]}$  in short) with a relatively short N–Si distance of about 1.75 Å [4].

In this paper the results of first-principles band structure calculations for the ternary nitride  $\text{Ba}_5\text{Si}_2\text{N}_6$  are presented. For a better understanding of the electronic structure of  $\text{Ba}_5\text{Si}_2\text{N}_6$ , it is useful to compare it with the electronic structure of the related binary nitride  $\text{Si}_3\text{N}_4$  ( $\text{N}^{[3]}$ ), as well as ternary nitrides  $\text{MgSiN}_2$  ( $\text{N}^{[2]}$ ) and  $\text{M}_2\text{Si}_5\text{N}_8$  ( $\text{N}^{[2]}$  and  $\text{N}^{[3]}$ ,  $\text{M}=\text{Ca}$  and Sr).  $\text{Si}_3\text{N}_4$  has two modifications [8,9]. Xu and Ching [10] performed band structure calculations for  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$  using the self-consistent orthogonal-

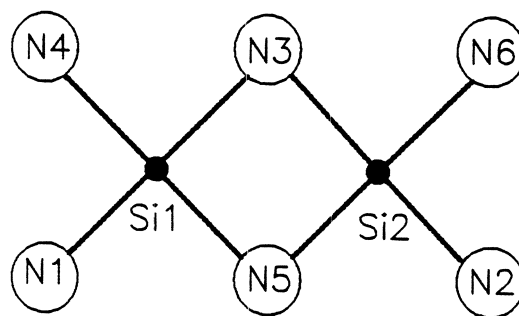


Fig. 1. The  $[\text{Si}_2\text{N}_6]^{10-}$  dimeric unit present in the crystal structure of  $\text{Ba}_5\text{Si}_2\text{N}_6$ . (After Yamane and DiSalvo [4]).

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ized linear combination of the atomic orbitals (OLCAO) method. They found that the electronic structures of  $\alpha$ - $\text{Si}_3\text{N}_4$  and  $\beta$ - $\text{Si}_3\text{N}_4$  are similar, and their results for  $\beta$ - $\text{Si}_3\text{N}_4$  are also in agreement to the calculations by Liu and Cohen using the first-principles pseudo-potential total energy approach within a localized orbital formalism [11]. The electronic structures of  $\text{MgSiN}_2$  [12] and  $\text{M}_2\text{Si}_5\text{N}_8$  ( $\text{M}=\text{Ca}$  and  $\text{Sr}$ ) [13] were calculated using the same method as used here.

Calculations were performed for  $\text{Ba}_5\text{Si}_2\text{N}_6$  with the Localized Spherical Wave (LSW) method [14] using a scalar-relativistic Hamiltonian. We used local-density exchange-correlation potentials (LDA) [15] inside space-filling, and therefore overlapping spheres around the atomic constituents. The self-consistent calculations were carried out including all core electrons. We performed iterations with 616  $\mathbf{k}$ -points distributed uniformly in an irreducible part of the Brillouin zone (BZ), corresponding to a volume of the BZ per  $\mathbf{k}$ -point of less than  $1 \times 10^{-6} \text{ \AA}^{-3}$ . Self-consistency was assumed when the changes in the local partial charges in each atomic sphere decreased to the order of  $1 \times 10^{-5}$ . Recently it was found that in ionic oxides (as alkali and alkaline earth oxides [16,17]) and nitrides (such as the binary nitride  $\text{Mg}_3\text{N}_2$  and the ternary nitrides  $\text{MgSiN}_2$  [12] and  $\text{M}_2\text{Si}_5\text{N}_8$  ( $\text{M}=\text{Ca}$  and  $\text{Sr}$ ) [13]), the anion 3s states have a strong influence on the values of calculated energy gaps and the characters of the conduction bands. Therefore, in the construction of the LSW basis [12,18], the spherical waves were augmented by solutions of the scalar-relativistic radial equations indicated by the atomic symbols 6s, 5p and 4d for Ba; 3s, 3p for Si, and 3s and 2p for N. The internal  $l$  summation used to augment a Hankel function at surrounding atoms was extended to  $l=2$ , resulting in the use of 3d orbitals for N and Si, and to  $l=3$ , resulting in the use of 4f orbitals for Ba. We also performed calculations with a basis set including N 2s orbitals. The Wigner–Seitz radius employed in the calculations is about 1.3  $\text{\AA}$  for N, 0.7  $\text{\AA}$  for Si, 1.4  $\text{\AA}$  for Ba. These radii of the spheres are close to the ionic radii [19]. Because the crystals of both nitrides are not very densely packed, it is necessary to include empty spheres in the calculations. The functions 1s and 2p, and 3d as an extension, were used for the empty spheres. The lattice parameters and coordinates of atoms used in these calculations are obtained from the single-crystal structure determination [4].

Fig. 2 shows the partial and total density of states (DOS) for  $\text{Ba}_5\text{Si}_2\text{N}_6$ . Table 1 lists the major features of the electronic structures of  $\text{Ba}_5\text{Si}_2\text{N}_6$  together with those of  $\text{Ca}_2\text{Si}_3\text{N}_8$  and  $\text{Sr}_2\text{Si}_5\text{N}_8$  [13], as well as of  $\text{MgSiN}_2$  [12] and  $\text{Si}_3\text{N}_4$  [10,11] for the sake of comparison.

As shown Fig. 2, the occupied states are mainly composed of the valence electrons (N 2p; Si 3s, 3p and Ba 6s states) and of the semicore level electrons (N 2s and Ba 5p states). The valence band, with a bandwidth of about 7.0 eV, is composed of mainly N 2p hybridized with Ba 6s

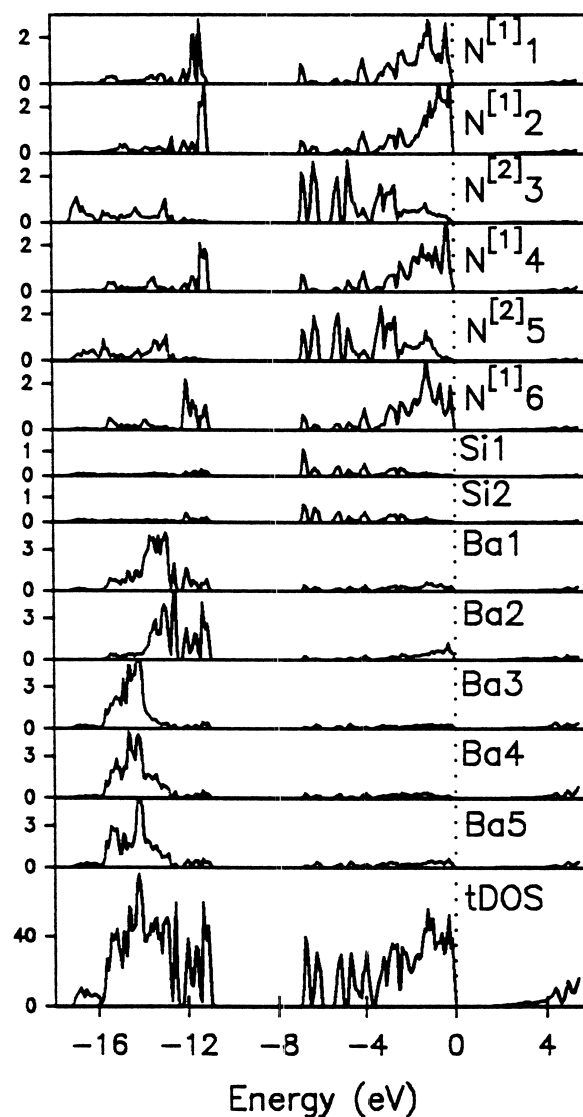


Fig. 2. Partial and total density of states of  $\text{Ba}_5\text{Si}_2\text{N}_6$  with N 2s in the basis set. The Y-axis has the unit (State/(eV·unit)). The Fermi level is set at 0 eV.

and Si 3s, 3p states. The Fermi level is set to be at the top of the valence band. The N 2p states are almost fully occupied, while the Si 3s and 3p states and Ba 6s states are almost empty. Therefore, at first approximation the crystal can be best described by the ionic model ( $\text{Ba}^{2+}$ ,  $\text{Si}^{4+}$  and  $\text{N}^{3-}$ ). In contrast to the electronic structures of the binary or ternary nitrides where the bands in the valence band have large dispersion (typically about 2–5 eV), there are some bands very narrow in the electronic structure of  $\text{Ba}_5\text{Si}_2\text{N}_6$  (typically about 0.5 eV). Moreover, there are two different shapes of the partial density of states for the nitrogen atoms in  $\text{Ba}_5\text{Si}_2\text{N}_6$ , corresponding to the two different types of N atoms ( $\text{N}^{[1]}$  and  $\text{N}^{[2]}$ , see Fig. 1 and Table 1). The lower part of the valence band (from about  $-7.0$  to  $-3.9$  eV) consists of narrow bands (about 0.3–0.5 eV, Fig. 2), which are composed of  $\text{N}^{[2]}$  2p states hybrid-

Table 1

Comparison of calculated electronic structure of  $\text{Ba}_5\text{Si}_2\text{N}_6$  ( $\text{N}^{[1]}$  and  $\text{N}^{[2]}$ ) with other alkaline-earth silicon nitrides:  $\text{MgSiN}_2$  ( $\text{N}^{[2]}$ ) [12],  $\text{M}_2\text{Si}_5\text{N}_8$  ( $\text{M}=\text{Ca}$  and  $\text{Sr}$ ,  $\text{N}^{[2]}$  and  $\text{N}^{[3]}$ ) [13], and  $\beta\text{-Si}_3\text{N}_4$  ( $\text{N}^{[3]}$ ) [10,11] (Data in parentheses represent the calculated energy gap without N 3s orbitals in the basis set)

	$\beta\text{-Si}_3\text{N}_4$ [11]	$\text{Ca}_2\text{Si}_5\text{N}_8$ [13]	$\text{Sr}_2\text{Si}_5\text{N}_8$ [13]	$\text{MgSiN}_2$ [12]	$\text{Ba}_5\text{Si}_2\text{N}_6$ (this work)
$d_{(\text{N}^{[1]}-\text{Si})}$ (Å)					1.75
$d_{(\text{N}^{[2]}-\text{Si})}$ (Å)		1.71	1.72	1.75	1.83
$d_{(\text{N}^{[3]}-\text{Si})}$ (Å)	1.73	1.76	1.77		
Top of VB	$\Gamma\text{-A}$	$\Gamma\text{-Y}$	$\Gamma, \text{Y}$	$\Gamma, \text{H}$	$\Gamma\text{-X}$
Bottom of CB	$\Gamma$	$\Gamma$	$\Gamma$	$\Gamma$	$\Gamma$
Position: $\text{N}^{[1]}$ 2p					−3.5 to 0.0
Width: $\text{N}^{[1]}$ 2p					3.5
Position: $\text{N}^{[2]}$ 2p		−5.7 to 0.0	−6.0 to 0.0	−6.5 to 0.0	−7.0 to 0.0
Width: $\text{N}^{[2]}$ 2p		5.7	6.0	6.5	7.0
Position: $\text{N}^{[3]}$ 2p	−9.8 to 0.0	−10.0 to −2.1	−9.7 to −1.0		
Width: $\text{N}^{[3]}$ 2p	9.8	7.9	8.7		
Position: $\text{N}^{[1]}$ 2s					−12.2 to −11.0
Width: $\text{N}^{[1]}$ 2s					1.1
Position: $\text{N}^{[2]}$ 2s		−14.5 to −11.8	−16.1 to −12.3	−15.5 to −12.3	−17.3 to −12.4
Width: $\text{N}^{[2]}$ 2s		2.7	3.8	3.2	4.9
Position: $\text{N}^{[3]}$ 2s	−18.2 to −14.0	−19.2 to −15.7	−19.5 to −15.9		
Width: $\text{N}^{[3]}$ 2s	4.2	3.5	4.0		
$E_{\text{g at } \Gamma}$ (eV)	5.25	4.35 (5.35)	3.32 (5.80)	4.35 (6.45)	0.8 (1.7)
$E_{\text{g min}}$ (eV)	4.96	4.10 (5.10)	3.32 (5.80)	4.35 (6.45)	0.7 (1.6)
$E_{\text{g}}$ (optical, eV)	4.6–5.5	4.9	4.5	4.8	~2

ized with Si 3s character. The top of the valence band is dominated by  $\text{N}^{[1]}$  2p states hybridized with some Si 3p states and Ba 6s states. Therefore, although predominately ionic, some covalent interaction exists between the nitrogen and the metal atoms. The small dispersion of the bands indicates localization of the N 2p and Si 3s, 3p states, corresponding to the fact that the structure of  $\text{Ba}_5\text{Si}_2\text{N}_6$  is zero-dimensional, with  $[\text{Si}_2\text{N}_6]^{10-}$  dimeric units [4].

The bandwidth of all 2p states of  $\text{N}^{[2]}$  (N3 and N5, Fig. 2) in  $\text{Ba}_5\text{Si}_2\text{N}_6$  is about 7.0 eV (Fig. 2), which is even larger than those in other ternary nitrides (Table 1). The 2p states of the  $\text{N}^{[1]}$  atoms (N1, N2, N4 and N6) which are dominant in the upper part of the valence band, have a smaller bandwidth of just about 3.5 eV, which is the narrowest band found for metal-silicon nitrides.

The partial density of the 2s states of the various nitrogen atoms also shows significant differences (Fig. 2). The  $\text{N}^{[1]}$  (N1, N2, N4 and N6) atoms in  $\text{Ba}_5\text{Si}_2\text{N}_6$  have a very narrow band of about 1.1 eV. On the other hand, the 2s states of the  $\text{N}^{[2]}$  (N3 and N5) atoms have rather dispersive bands, from −17.3 to −12.4 eV. The Ba 5p states also have rather broad bands (from −15.9 to −12.4 eV), in between the 2s states of the  $\text{N}^{[2]}$  atoms (Fig. 2). It is noted that there are some 5p states of Ba2 overlapping with the 2s states of the  $\text{N}^{[1]}$  atoms, in the energy range of −12.2 to −10.5 eV, corresponding to the fact that the Ba2 atom is tetrahedrally coordinated by  $\text{N}^{[1]}$  (N1, N2 and two N4) atoms [4]. Other Ba 5p states have different shapes of densities, corresponding to the different Ba–N coordination [4]. That indicates that although both N 2s and Ba 5p are regarded as semi-core level states, the interaction between the Ba 5p and N 2s is still significant. However, since both Ba 5p and N 2s states are fully occupied, the

overlaps between them do not contribute to the chemical bonding of the crystal.

The bottom of the conduction band for  $\text{Ba}_5\text{Si}_2\text{N}_6$ , mainly composed of Ba 6s states, is at  $\Gamma$ . The Si 3s states are positioned higher in energy. The top of the valence band is along the  $\Gamma\text{-X}$  line. Therefore, in this basis set  $\text{Ba}_5\text{Si}_2\text{N}_6$  is calculated to be a semiconductor with an indirect energy gap of 1.6 eV.

Table 1 also shows the calculated results with N 3s orbitals included in the basis set for  $\text{Ba}_5\text{Si}_2\text{N}_6$ . There are hardly any differences between the two valence bands calculated with/without N 3s in the basis set. However, the bottom of the conduction band contains now both Ba 6s and N 3s characters. Also the calculated band gap is about 0.7 eV, significantly smaller than that found for the calculations without N 3s states in the basis set, as found for other nitrides [12,13].

For the alkaline-earth silicon nitride  $\text{Ba}_5\text{Si}_2\text{N}_6$ , until now no experimental data about the electronic properties have been reported. The  $\text{Ba}_5\text{Si}_2\text{N}_6$  samples have a transparent reddish-brown color [4], from which the energy gap is deduced to be about 2 eV. The calculated direct band gap at  $\Gamma$  of about 0.8 eV (with N 3s in the basis set, or 1.7 eV without N 3s in the basis set) is in fair agreement with this estimated experimental value, considering the fact that the local density approximation employed in our calculations generally underestimates the energy gaps for semiconductors [20].

In summary, first-principles band structure calculations were performed for the ternary alkaline-earth silicon nitride  $\text{Ba}_5\text{Si}_2\text{N}_6$ . Both the zero-dimensionality of the  $[\text{Si}_2\text{N}_6]^{10-}$  dimeric units present in the structure and the coordination number of nitrogen by silicon show strong

influences on the partial electronic structure of these atoms. The interaction between the semicore-level states Ba 5p and N 2s is significant. The calculations also show that the conduction bands are determined by N 3s states hybridized with Ba 6s states. The calculations show that the compound is a semiconductor with an indirect energy gap of about 0.7 eV.

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